We Claim:

1. A process for the production of lower aliphatic esters said process comprising reacting a lower olefin with a saturated lower aliphatic mono-carboxylic acid in the vapour phase in the presence of a heteropolyacid catalyst characterised in that an amount of water in the range from 1-10 mole % based on the total of the olefin, aliphatic mono-carboxylic acid and water is added to the reaction mixture during the reaction.

2. A process according to Claim 1 wherein the amount of water added is in the range from 1 to 7 mole % based on the total of the olefin, aliphatic mono-carboxylic acid and water.

3. A process according to Claim 1 wherein the amount of water added is in the range from 1 to 5 mole % based on the total of the olefin, aliphatic mono-carboxylic acid and water.

4. A process according to Claim 1 wherein the heteropolyacid catalyst is supported on a siliceous support which is in the form of extrudates or pellets.

5. A process according to Claim 4 wherein the siliceous support is derived from an amorphous, non-porous synthetic silica.

6. A process according to Claim 4 wherein the siliceous support is derived from fumed silica produced by flame hydrolysis of $SiCl_4$.

7. A process according to Claim 4 wherein the siliceous supports is Support 350 made by pelletisation of AEROSIL® 200 (both ex Degussa).

8. A process according to Claim 4 wherein the silica support is in the form of pellets or beads or are globular in shape having an average particle diameter in the range from 2 to 10 mm, a pore volume in the range from 0.3-1.2 ml/g, a crush strength of at least 2 Kg force and a bulk density of at least 380 g/l.

9. A process according to Claim 4 wherein the siliceous support has at least 99%

w/w purity.

10. A process according to Claim 4 wherein the siliceous support is a pelleted silica support which has an average bulk density of about 0.39 g/ml, an average pore volume of about 1.15 ml/g and an average particle size ranging from about 0.1-3.5 mm.

11. A process according to Claim 10 wherein the pelleted silica support is used as such or after crushing to an average particle size in the range from 0.5-2 mm to support the heteropolyacid catalyst.

12. A process according to Claim 1 wherein the heteropolyacids used to prepare the esterification catalyst is selected from the free acids and co-ordination-type salts thereof in which the anion is a complex, high molecular weight entity and comprises 2-18 oxygen-linked polyvalent metal peripheral atoms surrounding in a symmetrical manner a central atom or ion from Groups I-VIII in the Periodic Table of Elements.

13. A process according to Claim 12 wherein the peripheral atom is one or more of molybdenum, tungsten, vanadium, niobium and tantalum and the central atom or ion is selected from silicon; phosphorus; cupric ions; divalent beryllium, zinc, cobalt or nickel ions; trivalent boron, aluminium, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium or rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulphur, tellurium, manganese nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium, antimony ions; hexavalent tellurium ions; and heptavalent iodine ions.

14. A process according to Claim 1 wherein the heteropolyacids have a molecular weight eg in the range from 700-8500 and include dimeric complexes.

15. A process according to Claim 1 wherein the heteropolyacid comprises at least one of the following compounds:

| | | |
|---|---|---|
| 12-tungstophosphoric acid | - | $H_3[PW_{12}O_{40}].xH_20$ |
| 12-molybdophosphoric acid | - | $H_3[PMo_{12}O_{40}].xH_2O$ |
| 12-tungstosilicic acid | - | $H_4[SiW_{12}O_{40}].xH_2O$ |
| 12-molybdosilicic acid | - | $H_4[SiMo_{12}O_{40}].xH_2O$ |
| Potassium tungstophosphate | - | $K_6[P_2W_{18}O_{62}].xH_2O$ |
| Sodium molybdophosphate | - | $Na_3[PMo_{12}O_{40}].xH_2O$ |
| Ammonium molybdodiphosphate | - | $(NH_4)_6[P_2Mo_{18}O_{62}].xH_2O$ |
| Sodium tungstonickelate | - | $Na_4[NiW_6O_{24}H_6].xH_2O$ |
| Ammonium molybdodicobaltate | - | $(NH_4)[Co_2Mo_{10}O_{36}].xH_2O$ |
| Cesium hydrogen tungstosilicate | - | $Cs_3H[SiW_{12}O_{40}].xH_2O$ |
| Potassium molybdodivanado phosphate | - | $K_5[PMoV_2O_{40}].xH_2O$ |



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16. A process according to Claim 4 wherein the amount of heteropolyacid deposited/impregnated on the support for use in the esterification reaction is in the range from 10 to 60% by weight based on the total weight of the heteropolyacid and the support.

17. A process according to Claim 1 wherein the olefin reactant used is ethylene, propylene or mixtures thereof.

18. A process according to Claim 1 wherein the saturated, lower aliphatic mono-carboxylic acid reactant is a C1-C4 carboxylic acid.

19. A process according to Claim 1 wherein the aliphatic mono-carboxylic acid reactant is acetic acid.

20. A process according to Claim 1 wherein the reaction mixture has a molar excess of the olefin reactant with respect to the aliphatic mono-carboxylic acid reactant.

21. A process according to Claim 1 wherein the mole ratio of olefin to the lower carboxylic acid in the reaction mixture is in the range from 1:1 to 15 : 1.

22. A process according to Claim 1 wherein the mole ratio of olefin to the lower carboxylic acid in the reaction mixture is in the range from 10:1 to 14:1.

23. A process according to Claim 1 wherein the reaction is carried out in the vapour phase above the dew point of the reactor contents comprising the reactant acid, any alcohol formed *in situ*, the product ester and water.

24. A process according to Claim 1 wherein the supported heteropolyacid catalyst is used as a fixed bed which is in the form of a packed column.

25. A process according to Claim 1 wherein the heteropolyacid catalyst is further modified by the addition of phosphoric acid or other mineral acids thereto.

26. A process according to Claim 1 wherein the vapours of the reactant olefins and acids are passed over the catalyst at a GHSV in the range of 100 to 5000 per hour.

27. A process according to Claim 1 wherein the esterification reaction is carried out at a temperature in the range from 150-200°C using a reaction pressure which is at least 400KPa.

28. A process according to Claim 1 wherein the reaction mixture is dosed with a di-ether amount of a di-ether co-fed is suitably in the range from 1 to 6 mole % based on the total reaction mixture comprising the olefin, the aliphatic carboxylic acid, water and di-ether.

29. A process according to Claim 28 wherein the di-ether corresponds to the



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by-product di-ether formed *in situ* during the reaction from the reactant olefin which is recovered and is recycled to the reaction mixture.

A process according Claim 24 wherein the di-ether is diethyl ether.

A process according to Claim 24 wherein the di-ether is an unsymmetrical ether.



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